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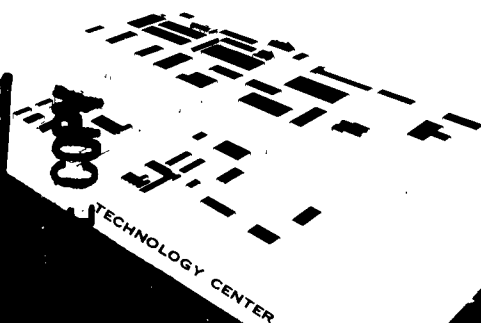
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ARMOUR RESEARCH FOUNDATION OF ILLINOIS INC.



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Report No. ARF-C6001-4
(Progress Report)

**PREPARATION AND EVALUATION
OF NEW HYDRAULIC FLUIDS**

Bureau of Ships
Washington 25, D. C.

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

(4) #1.10

(5) 75 900

SAAD-401 055

(14)
~~Report No. ARF-C6001-4~~
(9) Progress Report

(6) PREPARATION AND EVALUATION OF NEW HYDRAULIC FLUIDS. (7) NA

(8) February (28) through March (27) 1963, (10) (See p-8)

Bureau of Ships
Washington 25, D. C.

(11) 27 Mar 63, (12) 9 p.

(15) Contract ~~NS~~ NObs 88249, (13) NA
(16) ARF Project C6001

(17) (18) NA

(20) V (21) NA

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I. INTRODUCTION

The purpose of this project is to develop new fire-resistant hydraulic fluids based on fluorinated, sulfur-containing compounds. ^{are being developed} The compounds ^{are being} synthesized specifically to meet the critical property requirements. Various derivatives of sulfur hexafluoride and other fluorinated materials are being investigated under investigation.

The program consists of four phases: Simon's cell fluorinations, fluorinations with metallic fluorides, addition of sulfur chloride pentafluoride to olefins, and determination of physical and chemical properties.

II. RESEARCH PROGRAM

A. Simon's Cell Fluorinations

During the past month, a number of electrochemical fluorinations have been carried out in an attempt to prepare bisheptafluoropropylsulfur tetrafluoride, $(C_3F_7)_2SF_4$. The apparatus used for these reactions was fully described in Report No. ARF-C6001-3. Some difficulty was encountered in the preliminary electrolytic fluorinations. A leak in the system permitted hydrogen fluoride to escape, and a short circuit across the electrodes was

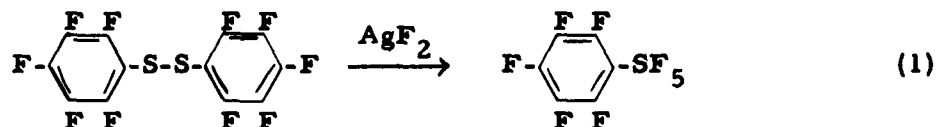
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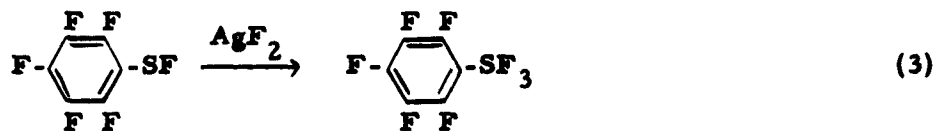
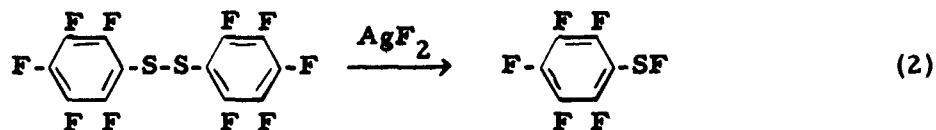
also observed. The leak has now been repaired. To eliminate the short circuit, the nickel rods connecting the electrodes were coated with wax. It is now possible to run the cell at 5 volts for 2 hours. The voltage then drops to 3 volts and remains at that value for the remainder of the experiment (200 minutes). About 3 ml of bisheptafluoropropylsulfur tetrafluoride was obtained by the electrolysis of 10 ml of n-butylsulfide in 100 ml of hydrogen fluoride. Since, a larger amount of this material is now being obtained from F. W. Hoffmann of the Army Chemical Center, Maryland, there is no need for further work on the preparation of this compound.

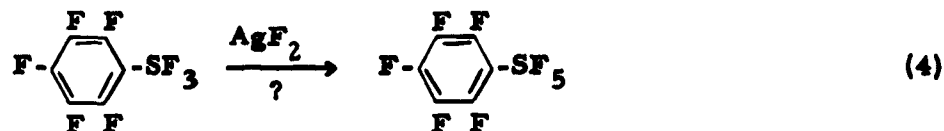
B. Fluorination with Metallic Fluorides

The preparation of pentafluorosulfur pentafluorobenzene, $C_6F_5SF_5$, is being attempted as shown in Equation (1).



The preparation of the starting material was described in Report No. ARF-C6001-2. This reaction was first run with a 2:1 mole ratio of silver difluoride to decafluorodiphenyldisulfide, and the reaction mixture was heated to 130°C for 2 hours. Apparently the reaction proceeds in three steps:





Reactions 2 and 3 are rapid, whereas reaction 4 is slower. It was realized that a larger amount of silver difluoride was needed to convert all the disulfide to pentafluoro sulfur pentafluorobenzene; but only a small amount of the fluorinating agent was used in order to minimize cleavage of the desired product. However, the NMR spectrum of the product showed very little, if any, of the desired $\text{C}_6\text{F}_5\text{SF}_5$. The majority of the product was probably the intermediate $\text{C}_6\text{F}_5\text{SF}_3$.

The reaction has now been repeated with a 6:1 mole ratio of silver difluoride to decafluorodiphenyldisulfide and a shorter reaction time (1/2 hour) to minimize degradation of the product. The products are now being analyzed and the results will be given in the next report.

C. Addition of Sulfurchloride Pentafluoride to Olefins

1. Preparation of Sulfurchloride Pentafluoride

Sulfurchloride pentafluoride is prepared in two steps:



First chlorine trifluoride and chlorine are heated to 350°C to produce chlorine monofluoride. Then sulfur tetrafluoride is introduced into the system. The resultant product, which is approximately 95% pure, is contaminated with about 5% sulfur hexafluoride. The sulfurchloride pentafluoride may be purified further by either a low-temperature or a high-pressure distillation. However, it is believed that the impure sulfurchloride penta-

fluoride can be allowed to react with the respective olefin. Since sulfur hexafluoride is inert, it can be more easily removed after the reaction.

A setup for the preparation of sulfur chloride pentafluoride has been built but will not be used for the present. Approximately 400 g of this material has been obtained from N. H. Ray and H. L. Roberts of Imperial Chemical Industries, and this amount of starting material is anticipated to be sufficient for the first series of planned reactions.

2. Other Sulfur pentafluoride Derivatives

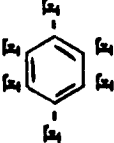
The personnel of Imperial Chemical Industries have been exceedingly generous in also supplying samples of the following materials: 4-chloro-octafluorobutylsulfur pentafluoride, 6-chloro-dodecafluorohexylsulfur pentafluoride, 4-chloro-octafluorobutylsulfur pentafluoride, and 4-chloro-butylsulfur pentafluoride. In addition, they supplied viscosity data for a number of other compounds of this type. These data, along with data obtained in our laboratories, are shown in Table 1. After additional data have been obtained, viscosity-structure correlations will be attempted.

D. Characterization of Sulfur Pentafluoride Compounds

The best and most convenient method for the characterization of sulfur pentafluoride compounds is nuclear magnetic resonance (NMR) spectroscopy. As an example, the NMR spectrum of 4-chloro-octafluorobutylsulfur pentafluoride is given in Figure 1. This spectrum shows the expected six lines. Since none of the CF_2 groups is completely equivalent to another, four separate lines are observed. These lines appear at the left side of the figure. The doublet is probably due to the two inner CF_2 groups, which are the more closely equivalent of the four groups. The other lines (one containing two peaks, the other five) are due to the SF_5 groups.

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Table 1
VISCOSITIES OF VARIOUS FLUORINATED MATERIALS

Compound	Viscosity, centistokes									
	75°C	71°C	60°C	50°C	38°C	25°C	23°C	0°C	-25°C	-50°C -75°C
			0.39	0.43	0.48	0.56				
$\text{CF}_3-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{CF}_2-\text{CF}_3$	0.44	0.50	0.58	0.68	0.85					
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{SF}_5$	0.30	0.31	0.34	0.38	0.44					
$\text{Cl}(\text{CH}_2)_4\text{SF}_5$		0.51	0.59	0.67	0.83					
$\text{CH}_3\text{CHClCH}_2\text{SF}_5$	0.47	0.99	1.16	1.38	1.83					
$\text{Cl}(\text{CF}_2)_2\text{SF}_5$				0.38	0.53	0.81	1.35	2.80		

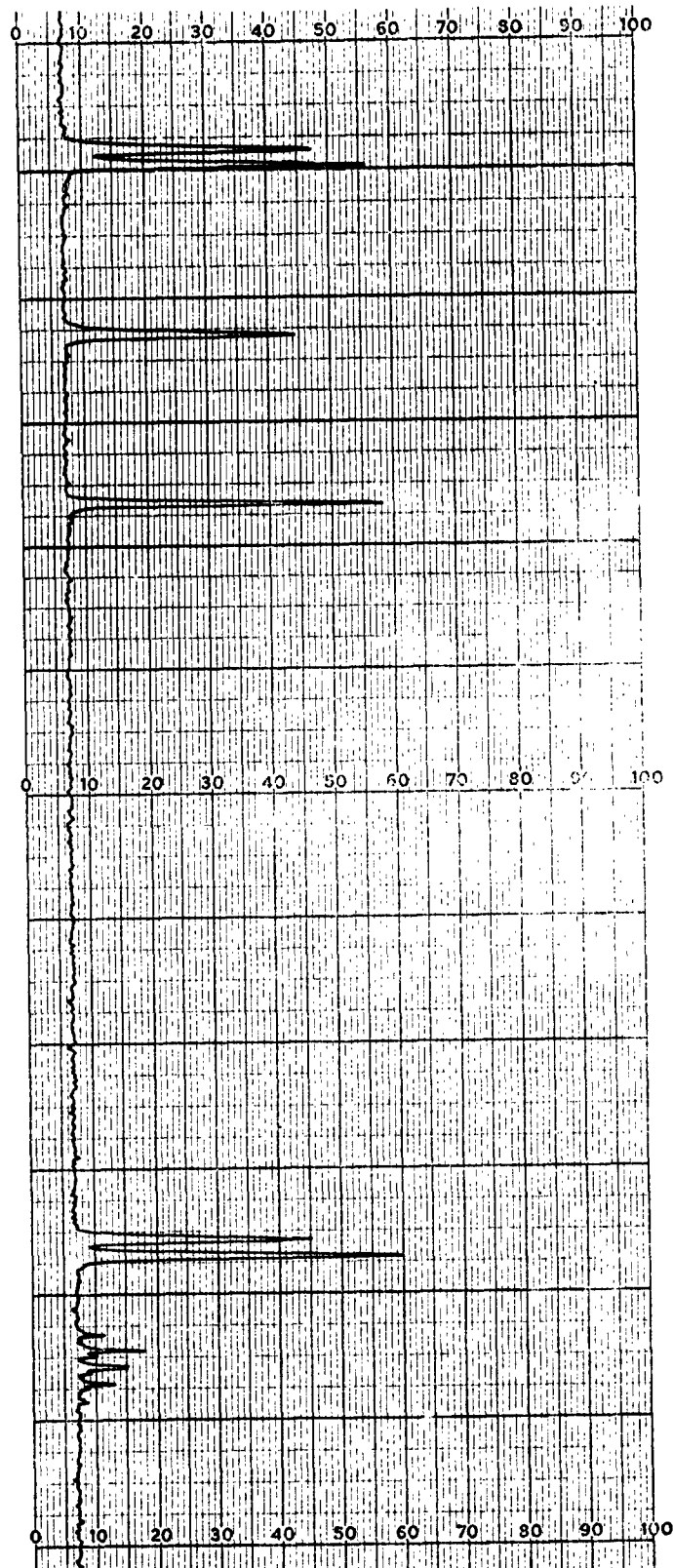


Figure 1
 NUCLEAR MAGNETIC RESONANCE SPECTRUM OF $\text{ClCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SF}_5$

This spectrum clearly shows the pyramidal structure of the SF_5 group (See Figure 2). Since there are four equivalent and one non-equivalent fluorines in this group, the spectrum should show two main lines with an intensity ratio of four to one. This is the case. The four planar fluorines correspondingly split the smallest line into four peaks, and the single apex fluorine splits the larger lines into two peaks. The chemical shifts for each line are:

$$CF_{2_a} - = 121.1 \text{ ppm}$$

$$CF_{2_b} - = 118.0 \text{ ppm}$$

$$CF_{2_c} - = 98.2 \text{ ppm}$$

$$CF_{2_d} - = 68.6 \text{ ppm}$$

$$SF_4 - = -40.7 \text{ ppm}$$

$$SF - = -58.4 \text{ ppm}$$

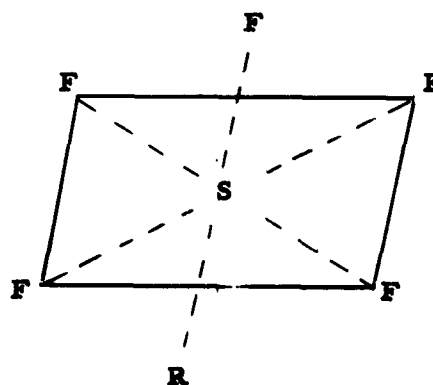


Figure 2

STRUCTURE OF SF_5 GROUP

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On all the compounds studied to date, the SF_5 group appears at the same place, and the spectrum is the same as that shown in Figure 1. Thus, the presence of SF_5 groups in new compounds can now be easily identified.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION
of Illinois Institute of Technology

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